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A Turn-Key FTIR System for the Analysis of Gas Phase Polychlorinated Biphenyls

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Abstract

A turn-key gas phase polychlorinated biphenyl analysis system has been developed using Fourier transform infrared spectrometry, artificial intelligence assisted library searching and an automated infrared interpreter. Vapor phase infrared spectra of 37 PCB isomers have been measured and used to define the interpretation rules. The library search algorithm and the infrared interpreter take advantage of the portability, computing power and mass data storage capability of PC/DOS systems and is demonstrated to be a cost effective tool to ensure consistent data interpretation. This turn-key system allows for rapid identification of complex PCB mixtures with elucidation of contributing PCB congeners.

Introduction

An automated infrared interpreter (PAIRS *) was developed on an IBM personal computer (PC) running under the Microsoft disk operating system (DOS). Details of this program and its application for the analysis of oils and greases is given elsewhere (1). Briefly stated, PAIRS * combines both artificial intelligence and library search capabilities to interpret the infrared spectra measured with a wide variety of spectrophtometers. The library search subprogram uses five main algorithms: absolute difference (AB); square of absolute difference (SQ); absolute difference of first derivative (AD); square of difference of first derivative (SD) and time domain cross correlation (FT). A sixth additional algorithm, the combined algorithm (CO) was developed combining the library search results from the first five algorithms resulting in a higher confidence level for the reported data.

An artificial intelligence approach to gas phase PCB analysis in PAIRS * has been devised which can identify different types of chlorinated benzene rings based on the position, intensity and full width at half maximum (FWHM) of the infrared bands in the spectrum. These information have been obtained from the spectra of 37 PCB isomers that we have measured. With the combination of a suitable GC column, appropriate GC experimental conditions and this program it may be possible to identify all 209 PCB isomers which may be present in the sample.

Experimental

Solutions of 37 individual PCB isomers (Ultra Scientific, Wellington, CIL) were prepared in iso-octane with an initial concentration of between 100-150 ppm. Table 1 gives the list of these PCB isomers. Solutions were further concentrated if the S/N ratio of the infrared spectrum was less than 5. A Nicolet 5SX (Madison, WI) FT-IR spectrometer equipped with an air cooled nichrome wire source and a medium range cryogenic HgCdTe detector (cut-off frequency at about 600 cm^{-1}) was used to measure the GC/FT-IR spectra. The gas chromatograph used was a Hewlett-Packard 5890 (Palo Alto, CA) equipped with an on column injector, a wide bore column (cross-linked methyl Silicon Gum, 25 m x 0.32 mm i.d. x 1.0 micrometer film thickness) and a flame ionization detector. The starting temperature on GC for di-, tri-, and tetra- isomers was set at 200 °C and for penta- and hexa- isomers it was set at 210 °C. An initial hold time of 0.5 minute on GC was used and temperature was ramped at a rate of 3 °C/min to 270 °C. The injector temperature was set at 250 °C. The dimensions of the light pipe used were 12 cm x

0.1 cm and was operated at 270 °C throughout the experiment. Interferograms were collected at a sampling rate of 50 kHz, obtaining infrared spectra with 8 cm^{-1} resolution. The Gram-Schmidt orthogonalization algorithm (2) was used to reconstruct gas chromatograph from the interferograms and the infrared spectra.

Results and Discussion

The structure of each polychlorinated biphenyl consist of two benzene rings in which one to ten hydrogen atoms can be substituted by chlorine atoms. Substitution of these chlorines will give rise to eighteen (including a benzene group for PCBs with one unsubstituted ring) different types of chlorinated benzene rings. For example when one chlorine atom is present in the structure of the PCB, three different isomers i.e., 2-mono, 3-mono, and 4-mono biphenyls are possible. When two chlorines are present, 6 different isomers i.e., 2,3-di, 2,4-di, 2,5-di, 2,6-di, 3,4-di and 3,5-di are possible etc. These eighteen types of substitutions give rise to different infrared bands in the spectral region 600 to 2100 cm^{-1}. Figure 1 illustrates the spectra for three of the 37 isomers. Using the 37 spectra, the characteristic infrared bands for each type were identified. The eighteen types of substitution and the characteristic infrared bands are given in Table 2. For each infrared band the averaged normalized intensity and the averaged estimated FWHM are given in the parenthesis. Each PCB isomer is a binary combination of any of these eighteen groups. For some groups the characteristic bands overlap, but at least one band for each group can be identified which is unique to that group.

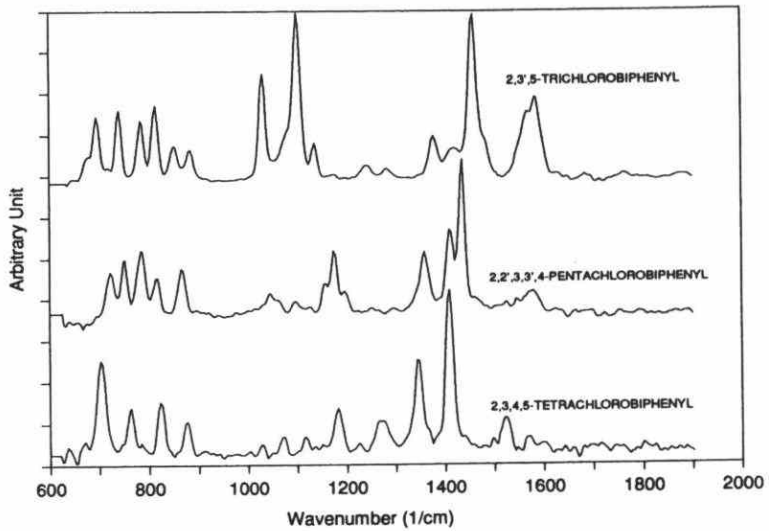

Fig. 1. Infrared gas phase spectrum of three PCB isomers.

Using the information given in Table 2, a program was written to interpret the data and identify the PCBs. This program requires three sets of information: 1) the spectral region of the bands pertinent to each group of PCB isomers where the algorithm will allow for the variations due to the types and the interaction between the two benzene rings, 2) a normalized intensity range from 1 to 10 where the bands will be considered as "weak" for the intensities in the range 1-2, "medium" between 3-6 and "strong" for the intensities between 7-10 and 3) an allowable range for the variation in the full width at half maximum (FWHM) of the bands

which will classify the bands as "sharp" for FWHM < 15 cm^{-1}, "medium" for FWHM of 15-30 cm^{-1} and "wide" for FWHM > 30 cm^{-1}. These information have been obtained from the analysis of the 37 vapor phase spectra of PCBs (see Table 2) and can be modified and/or changed in the program as required.

Conclusion

Gas phase infrared spectra of 37 PCB isomers have been measured and analyzed. The information obtained from these spectra are used in the elucidation of PCBs. Since these 37 isomers represent all the possible eighteen different types of substituted benzene rings in the polychlorinated biphenyl structure, it may be used to identify all 209 possible PCB isomers. This technique offers the possibility of direct environmental analysis by remote sensing and the potential for simplified analytical methodology through elimination of clean-up steps.

References

1. M.J. Yang and P.W. Yang, Appl. Spectrosc., in press (1991).
2. L.V. Azarraga and D.A. Hanna, GIFTS, Athens GC/FT-IR Software User's Guide, US EPA/ERL, Athens, GA, 1979.

Table 1- List of PCB isomers measured

Dichlorobiphenyls

1) 2,2'
2) 2,4'

Trichlorobiphenyls

3) 2,2',5
4) 2,3,4
5) 2',3,4
6) 2,3',5
7) 2,4,4'
8) 2,4,5
9) 2,4',5

Tetrachlorobiphenyls

10) 2,2',3,4'
11) 2,2',4,4'
12) 2,2',3,5
13) 2,2',3,5'
14) 2,2',4,6
15) 2,2',5,5'
16) 2,2',5,6'
17) 2,3,3',4
18) 2,3,4,4'
19) 2,3',4,4'
20) 2,3,4,5
21) 2',3,4,5
22) 2,3',4',5
23) 2,3',5,5'
24) 2,4,4',6
25) 2,3,5,6
26) 3,3',4,4'

Pentachlorobiphenyls

27) 2,2',3,3',4
28) 2,2'3,4,4'
29) 2,2',3',4,5
30) 2,2',3,4,5'
31) 2,2',4,5,6
32) 2,3,4,5,6
33) 2,3,4,4',5
34) 2'3,4,4',5

Hexachlorobiphenyls

35) 2,2',3,3',4,4'
36) 2,2',3,3',4,5
37) 2,2',3,3',5,6

Table 2- Characteristic infrared bands for different types of substituted benzene rings.

Type of Substitution	Characteristic ir band(s)
2	751(8[a],17[b]), 1038(4,18)
3	740(5,15), 783(4,19)
4	823(5,22), 1012(3,16), 1094(8,19)
2,3	726(5,20), 1409(7,21)
2,4	821(6,18), 869(2,20), 1103(6,18)
2,5	815(6,18), 1097(8,24), 1376(3,20)
2,6	783(9,27)
3,4	1035(6,22), 1134(6,24)
3,5	806(7,23), 1099(6,15), 1562(10,11)
2,3,4	784(5, 21), 817(4,19), 1174(4,21), 1358(4, 23)
2,3,5	1034(8,23), 1095(9,30)
2,4,5	886(4,20), 1045(4,28), 1091(4,23), 1139(4,23)
2,4,6	838(8,18), 1543(6,23), 1577(7,26)
3,4,5	810(5,19), 876(2,19)
2,3,4,5	1179(4,23), 1342(6,23)
2,3,5,6	1062(8,21), 1388(10,31)
2,3,4,5,6	1323(7,27), 1377(6,19)
Benzene ring	699(7,22)

[a] Intensity on the scale of 1 to 10, 1 being weakest and 10 being the strongest peak.

[b] Full Width at Half Maximum (FWHM).